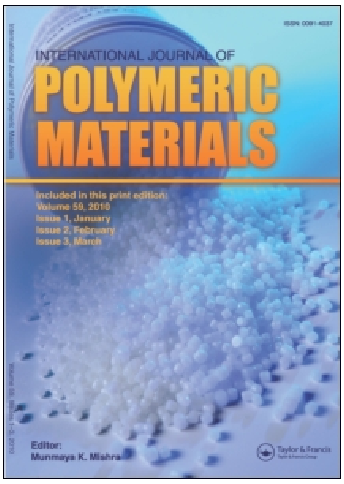

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Investigation of the Stabilizing Action of Mixtures of Fullerene C_{60} with Known Antioxidants in the Thermo-oxidative Degradation of Polystyrene

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To cite this Article Troitskii, B. B. , Troitskaya, L. S. , Anikina, L. I. , Denisova, V. N. , Novikova, M. A. and Khokhlova, L. V.(2001) 'Investigation of the Stabilizing Action of Mixtures of Fullerene C_{60} with Known Antioxidants in the Thermo-oxidative Degradation of Polystyrene', International Journal of Polymeric Materials, 48: 3, 251 — 265
To link to this Article: DOI: 10.1080/00914030108050785
URL: http://dx.doi.org/10.1080/00914030108050785

Intern. J. Polymeric Mater., 2001, Vol. 48, pp. 251–265
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Investigation of the Stabilizing Action of Mixtures of Fullerene C_{60} with Known Antioxidants in the Thermo-oxidative Degradation of Polystyrene

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(Received 7 October 1999; In final form 5 November 1999)

Investigations have been made on the effects of double mixtures of C_{60} with well-known antioxidants (amines, phenols, S- and P-containing compounds, Ph_3Sb) on the thermo-oxidative degradation of PS by DSC method under oxygen. The influence of mixtures on the temperature of the onset of polymer degradation, T_0, has been studied. The effects of concentration of C_{60} on the value of the temperature limit of inhibition of PS thermo-oxidative degradation by known antioxidants, T_0^{max}, have been investigated. It has been shown that mixtures of C_{60} with Ph_3Sb and phenyl-β-naphthylamine have a synergistic effect upon T_0. At a total concentration of 1.4×10^{-2} mol/kg, the maximum value of T_0 is observed at a molar C_{60} : compound ratio of 3 : 4 and 1 : 2.5 for the mixtures of C_{60} with Ph_3Sb and phenyl-β-naphthylamine, respectively. Addition of C_{60} to these compounds leads to an increase in T_0^{max} for Ph_3Sb and phenyl-β-naphthylamine. The suggestion was made that in the case of mixtures of C_{60} with Ph_3Sb, the synergistic effect is Associated with different mechanisms of stabilizing action of the components on PS degradation, namely C_{60} reacts with alkyl and oxygen-containing radicals with the formation of more stable compounds while Ph_3Sb decomposes polymeric and fullerene-containing peroxides and hydroperoxides. The decomposition of Ph_3Sb was investigated by DSC method under oxygen. The temperature of the onset of Ph_3Sb degradation was shown to be 362.5°C. It was concluded that further investigations are necessary for understanding the synergistic action of mixture of C_{60} with phenyl-β-naphthylamine in the thermo-oxidative degradation of PS.

*Corresponding author.

Keywords: Polystyrene; Thermo-oxidative degradation; Fullerene; Antioxidants; Synergism

1. INTRODUCTION

Recently [1–3], it has been shown that fullerene C_{60} retards the thermo-oxidative degradation of polystyrene (PS). By thermogravimetry, it was demonstrated that in the presence of fullerene, the induction periods of the curves of the dependence of weight loss of PS on time of degradation under oxygen raise substantially [1]. By a DSC method, it was illustrated that C_{60} increases considerably the temperature of the onset of polymer degradation [1–3].

This study deals with investigation by a DSC method of the effects of double mixtures of C_{60} with well-known antioxidants (aromatic and sterically hindered amines, sterically hindered phenols, S- and P-containing compounds and triphenylstibine) on the thermo-oxidative degradation of PS.

2. EXPERIMENTAL

2.1. Materials

PS was prepared by bulk polymerization as described before [1].

The method of preparation and purification of fullerene C_{60} was published previously [4].

The following stabilizers have been used: Tinuvin 622 (Ciba-Geigy), Chimassorb 944 (Ciba-Geigy), phenyl-β-naphthylamine (Neozone D, Bayer), S-47, S-49, Si-phenol, dilauryl thiodipropionate (DLTP), dinaphthyl thiodipropionate (DNTP), tri(p-nonylphenyl) phosphite (Polygard, Naugatuck). Their chemical structures and constants are represented in [4]. Triphenylstibine (Ph_3Sb) was prepared by known method, m.p. 52–54°C, b.p. 220°C/12 mm Hg. Its constants agreed with literature values.

2.2. Methods

The degradation of PS films was carried out by a DSC method in dynamic oxygen (40 ml/min) at 100–400°C with scanning rate of

5°C/min. A charge of $1.0 \times 10^{-6} - 3.0 \times 10^{-6}$ kg of PS was used for each experiment. A DSC-7 Perkin-Elmer instrument was used. Films of PS without stabilizers and with additives were prepared as described previously [1].

The degradation of Ph_3Sb was investigated by a DSC method in dynamic oxygen. A charge of 1.0×10^{-6} kg of compound was used for the experiment.

3. RESULTS AND DISCUSSION

It is known [6] that synergistic action of mixtures of compounds is observed when there is maximum on the curve of the dependence of any property on the ratio of components at constant total concentration of mixture. We investigated the influence of double mixtures of fullerene C_{60} with different antioxidants on the temperature of the onset of thermo-oxidative degradation of PS, T_0. The values of T_0 were determined using DSC curves of the degradation of PS in dynamic oxygen. The DSC curves for the thermo-oxidative degradation of PS alone and in the presence of C_{60} and well-known antioxidants have been represented and discussed previously [1 – 3, 5].

Figure 1 shows the dependence of T_0 on C_{60}: compound ratio at a total concentration of 1.4×10^{-2} mol/kg for the double mixtures of C_{60} with sterically hindered phenol, Si-phenol (c); sterically hindered amine, Chimassorb 944 (d); aromatic amines: phenyl-β-naphthylamine (b), S-47 (e), S-49 (f); S-containing compounds: DLTP (g), DNTP (h) and Ph_3Sb (a) in the thermo-oxidative degradation of PS. It is seen that only mixtures of C_{60} with phenyl-β-naphthylamine (Fig. 1b) and Ph_3Sb (Fig. 1a) have a synergistic effect upon T_0. The maximum value of T_0 is observed at a molar C_{60}: compound ratio of 3 : 4 and 1 : 2.5 for the mixtures of C_{60} with Ph_3Sb and phenyl-β-naphthylamine, respectively.

The temperature limit of effective inhibition of the thermo-oxidative degradation of polymer is an important characteristic of a stabilizer. Recently, the temperature limits of effective inhibition of the thermo-oxidative degradation of PS and PMMA by C_{60} [2, 3] and by known antioxidants [2, 5] have been determined using the dependence of T_0 on concentration of a stabilizer. Beginning with definite concentration of an additive, the maximum value of T_0, T_0^{max}, is observed. The value of T_0^{max} changes slightly with further increase in an antioxidant

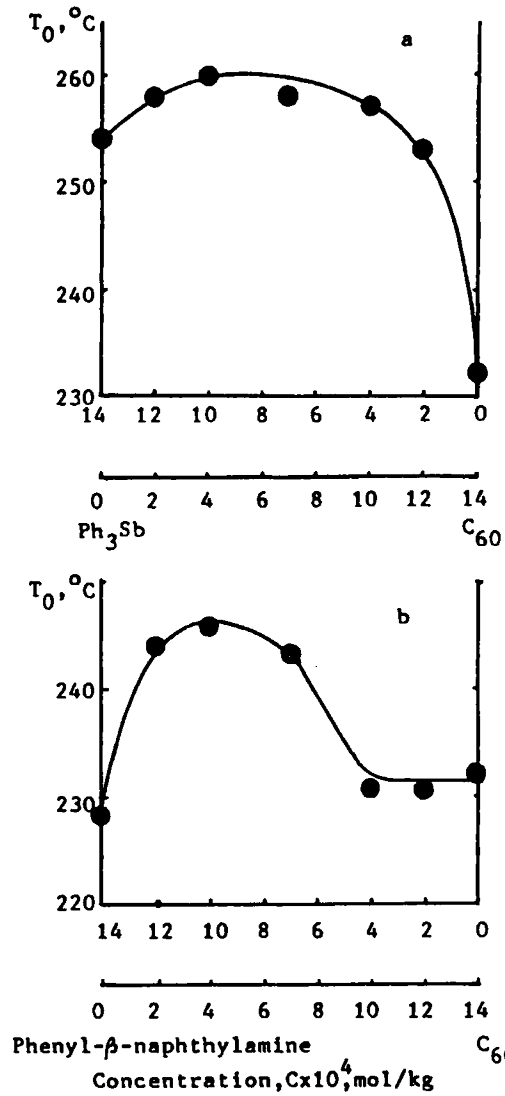


FIGURE 1 Dependence of T_0 on C_{60}: compound ratio at a total concentration of 1.4×10^{-2} mol/kg in the thermo-oxidative degradation of PS. (a) Ph_3Sb; (b) phenyl-β-naphthylamine; (c) Si-phenol; (d) Chimassorb 944; (e) S-47; (f) S-49; (g) DLTP; (h) DNTP.

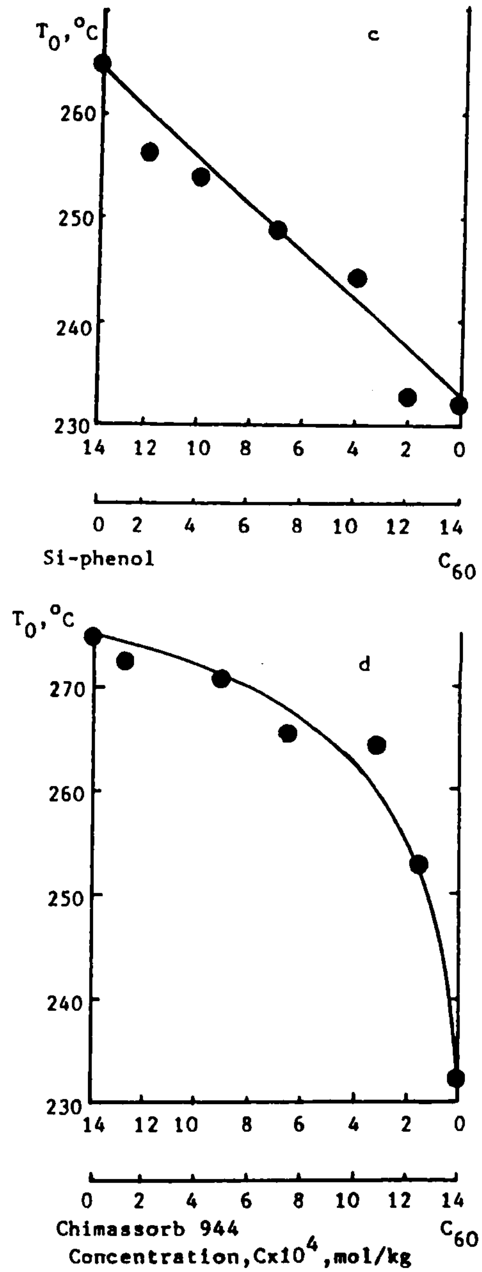
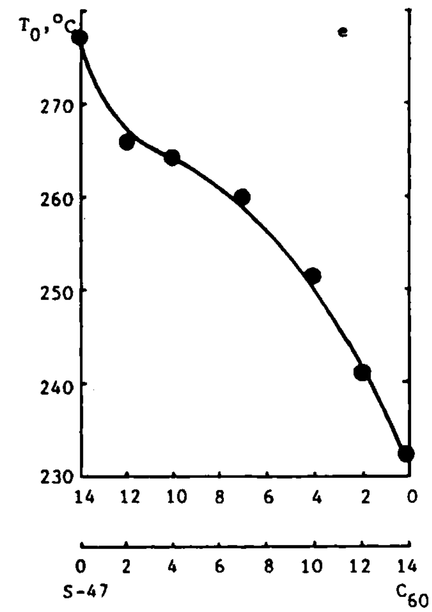


FIGURE 1 (Continued).



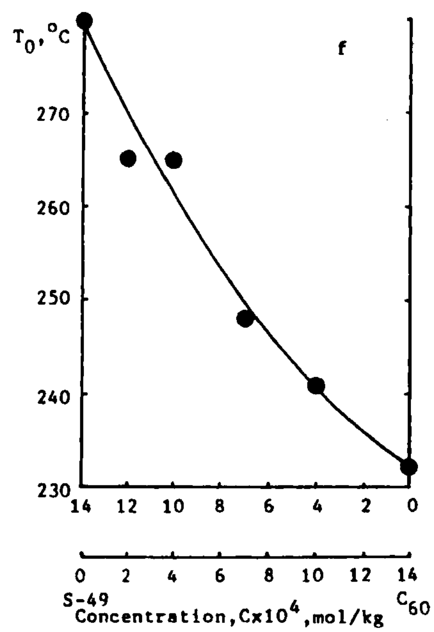


FIGURE 1 (Continued).

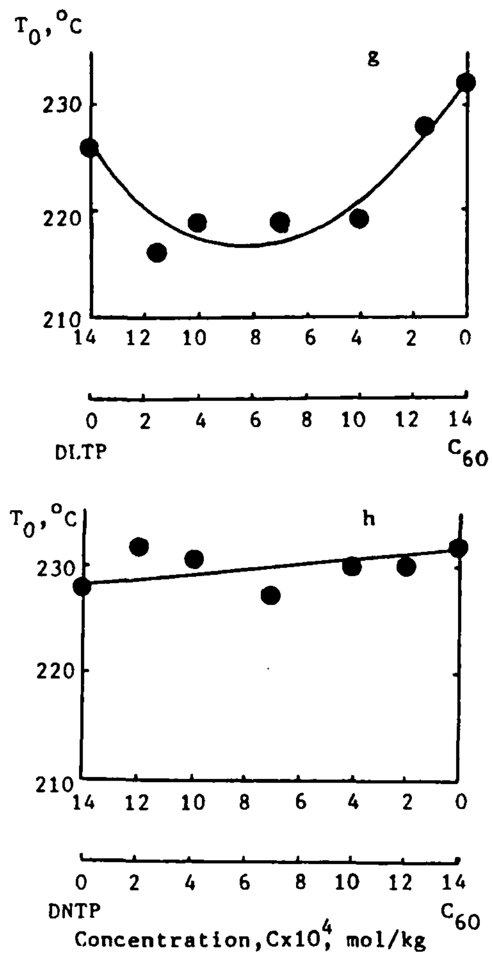


FIGURE 1 (Continued).

concentration. The value of T_0^{max} is the temperature limit of effective inhibition of the thermo-oxidative degradation of polymer by a stabilizer. It has been shown [2, 5] that the upper temperature limit of inhibition of the thermo-oxidative degradation of polymers by well-known effective antioxidants investigated, is in the range 280–295°C and depends insignificantly on the chemical structure of the polymer. Some known antioxidants are not effective at lower temperatures [5]. The degradation of antioxidants themselves was studied by DSC method in oxygen under conditions identical to those employed in the degradation of the polymers [2, 5]. The suggestion was made that the value of the temperature limit of inhibition of the thermo-oxidative degradation of polymers depends to a great extent on intensive oxidative decomposition of the antioxidant itself [2, 5].

It has been shown [2, 3] that under oxygen C_{60} begins to oxidize at 386°C. This temperature is much higher than that for other well-known antioxidants. It was concluded [2, 3] that in comparison with well-known antioxidants, fullerene C_{60} has considerable advantage as high temperature stabilizer for polymers.

For the case of C_{60}, the temperature limit of effective inhibition depends on the chemical structure of polymer. It is much lower in the aging of less stable PS and considerably greater in the degradation of more stable PMMA than that in the case of well-known antioxidants [2, 3]. It has been proposed that the thermo-oxidative aging of polymers initiates the oxidation of fullerene [2, 3]. In the presence of C_{60}, $T_0^{max} \cong 245°C$ in degradation of PS.

In this study, we investigated the influence of a concentration of C_{60} on the value of T_0^{max} in the thermo-oxidative degradation of PS in the presence of different antioxidants. Figures 2–9 represent the

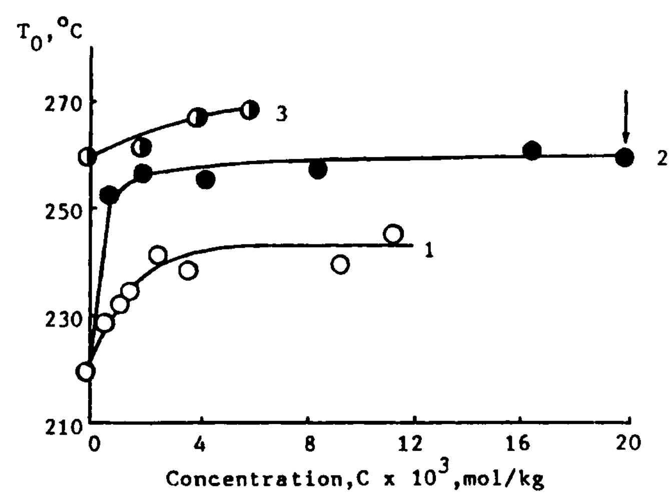


FIGURE 2 Dependence of T_0 on concentration of C_{60} (1), Ph_3Sb (2) and C_{60} in the presence of 2×10^{-2} mol/kg Ph_3Sb (3) in the thermo-oxidative degradation of PS.

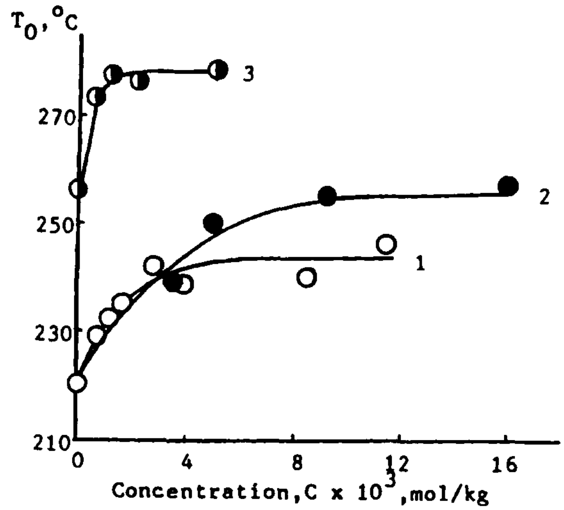


FIGURE 3 Dependence of T_0 on concentration of C_{60} (1), phenyl-β-naphthylamine (2) and C_{60} in the presence of 2.3×10^{-2} mol/kg phenyl-β-naphthylamine (3) in the thermo-oxidative degradation of PS.

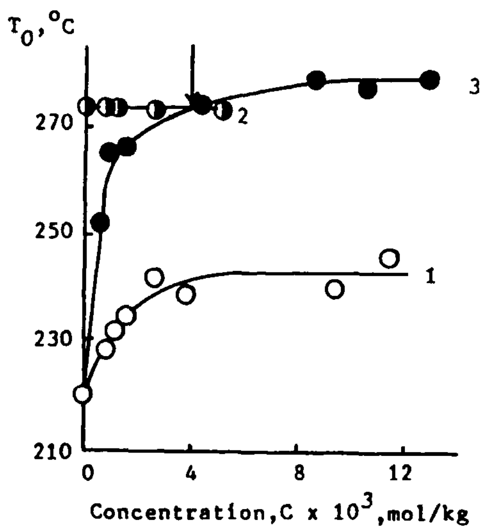


FIGURE 4 Dependence of T_0 on concentration of C_{60} (1), C_{60} in the presence of 3.9×10^{-3} mol/kg Si-phenol (2) and Si-phenol (3) in the thermo-oxidative degradation of PS.

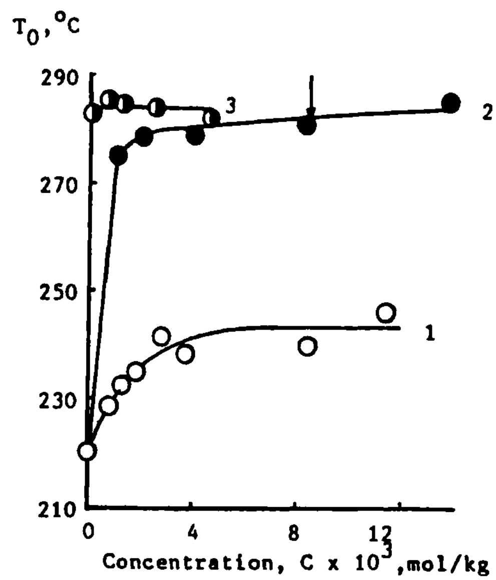


FIGURE 5 Dependence of T_0 on concentration of C_{60} (1), Chimassorb 944 (2) and C_{60} in the presence of 8.4×10^{-3} mol/kg Chimassorb 944 (3) in the thermo-oxidative degradation of PS.

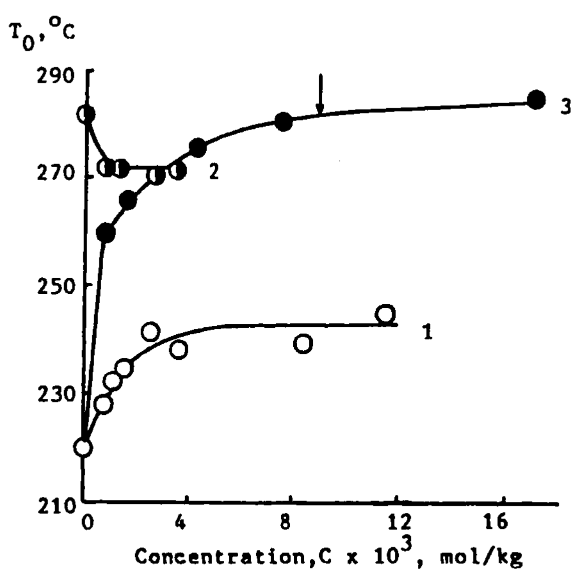


FIGURE 6 Dependence of T_0 on concentration of C_{60} (1), C_{60} in the presence of 8.9×10^{-3} mol/kg Tinuvin 622 (2) and Tinuvin 622 (3) in the thermo-oxidative degradation of PS.

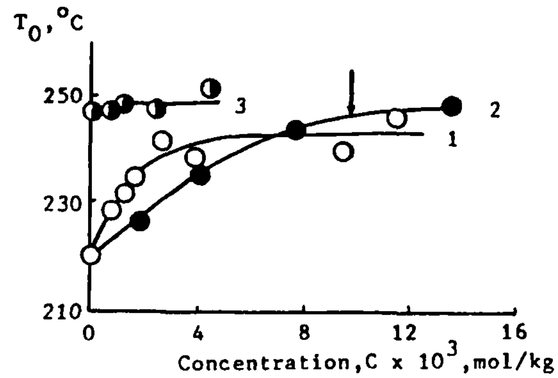


FIGURE 7 Dependence of T_0 on concentration of C_{60} (1), DLTP (2) and C_{60} in the presence of 9.7×10^{-3} mol/kg DLTP (3) in the thermo-oxidative degradation of PS.

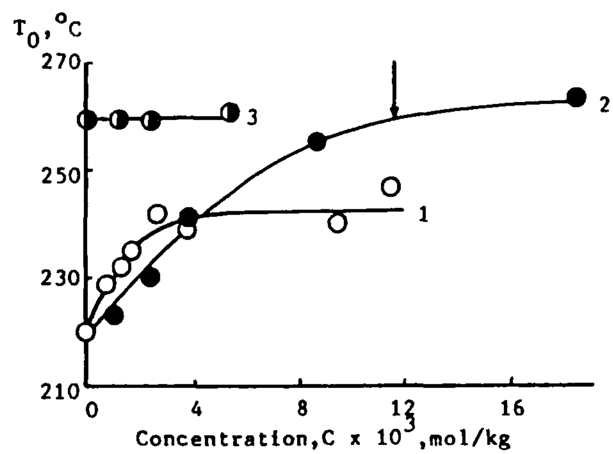


FIGURE 8 Dependence of T_0 on concentration of C_{60} (1), DNTP (2) and C_{60} in the presence of 1.16×10^{-2} mol/kg DNTP (3) in the thermo-oxidative degradation of PS.

dependence of T_0 on concentration of C_{60} and various antioxidants such as sterically hindered phenol, Si-phenol (Fig. 4, curves 1 and 3); sterically hindered amines: Chimassorb 944 (Fig. 5, curves 1 and 2) and Tinuvin 622 (Fig. 6, curves 1 and 3); aromatic amine, phenyl-β-naphthylamine (Fig. 3, curves 1 and 2); S-containing compounds: DLTP (Fig. 7, curves 1 and 2) and DNTP (Fig. 8, curves 1 and 2); P-containing compound, Polygard (Fig. 9, curves 1 and 2) and Ph_3Sb

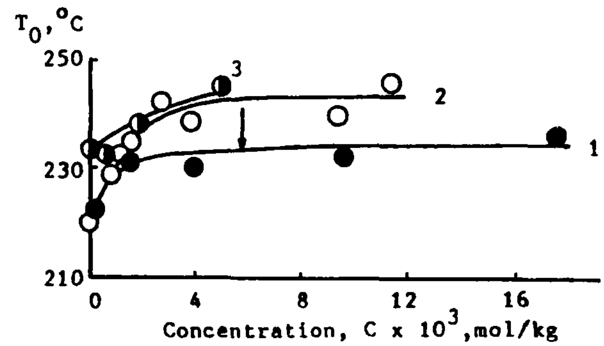


FIGURE 9 Dependence of T_0 on concentration of Polyhard (1), C_{60} (2) and C_{60} in the presence of 5.8×10^{-3} mol/kg Polyhard (3) in the thermo-oxidative degradation of PS.

(Fig. 2, curves 1 and 2). Figures 2–9 also demonstrate the dependence of T_0 on concentration of C_{60} in the presence of known antioxidant at the concentration when T_0^{max} is observed for the latter. This concentration of antioxidant is indicated by arrows in Figures 2–9. The latter dependence shows the influence of concentration of C_{60} on the value of T_0^{max} in the thermo-oxidative degradation of PS in the presence of known antioxidants. From Figures 2–9, it is seen that C_{60} increases the value of T_0^{max} only in the case of phenyl-β-naphthylamine (Fig. 3) and Ph_3Sb (Fig. 2).

Thus, it has been shown that double mixtures of C_{60} with phenyl-β-naphthylamine and Ph_3Sb have synergistic action in the thermo-oxidative degradation of PS.

Some kinds of synergistic mixtures are known in the thermo-oxidative degradation of polymers [6–8]. Synergistic mixtures of antioxidants which react with alkyl and oxygen-containing radicals, with compounds which decompose hydroperoxides, are widely used [6–8]. It may be proposed that the mixture of C_{60} with Ph_3Sb is such synergistic mixture. In the case of the mixture of C_{60} with Ph_3 Sb, the synergistic effect is connected with different mechanisms of stabilizing action of the components in PS degradation. It is well known [9, 10] that C_{60} reacts easily with low molecular weight alkyl radicals with the formation of remarkably persistent products and with oxygen-containing radicals. It has been supposed [1–3] that in the thermo-oxidative degradation of polymers, the inhibiting effect of C_{60} is due to its interaction with alkyl and oxygen-containing radicals with the

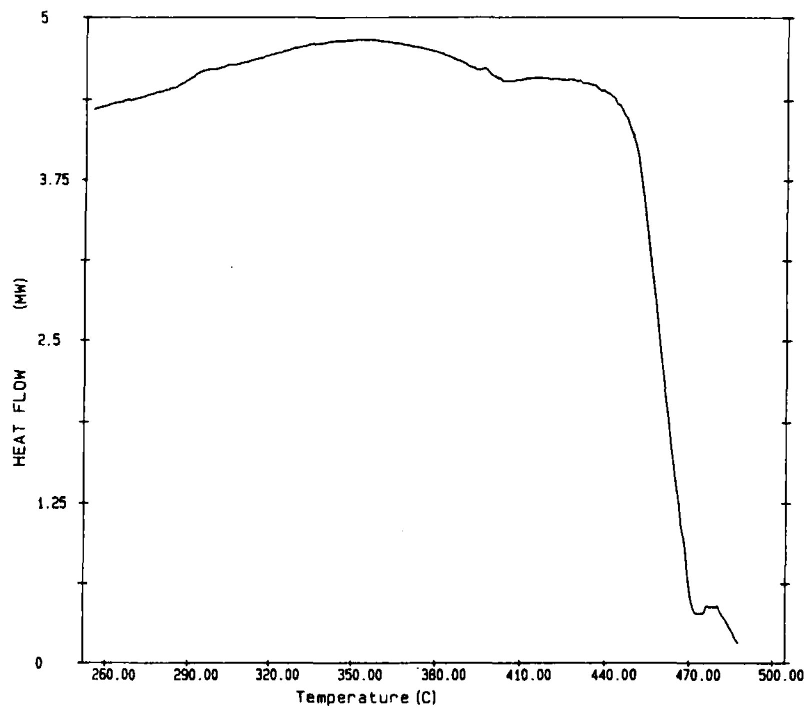


FIGURE 10 DSC curve (oxygen, 5°C/min) for Ph_3Sb.

formation of more stable compounds:

$$RO_2^{\bullet}(RO^{\bullet}, R^{\bullet}) + C_{60} \rightarrow RO_2\dot{C}_{60}(RO\dot{C}_{60}, R\dot{C}_{60}) \tag{1}$$

It has been shown that Ph_3Sb reacts easily with hydroperoxides [11, 12] and peroxides [13]:

$$Ph_3Sb + ROOH \rightarrow Ph_3SbO + ROH \tag{2}$$

It may be suggested that in the case of a mixture of C_{60} with Ph_3Sb, fullerene reacts with alkyl and oxygen-containing radicals and Ph_3Sb decomposes polymeric and fullerene-containing peroxides and hydroperoxides.

It is of interest to note that mixtures of C_{60} with well-known antioxidants which decompose hydroperoxides such as P-containing compound, Polyhard (Fig. 9), S-containing compounds: DLTP (Figs. 1g and 7) and DNTP (Figs. 1h and 8), have no synergistic action in the thermo-oxidative degradation of PS at high temperatures. These antioxidants are less stable than Ph_3Sb. It has been shown [5] that the temperatures of the onset of the thermo-oxidative degradation of Polyhard, DLTP and DNTP agree closely with the values of T_0^{max} for these compounds (see Figs. 9, 7 and 8, respectively). We have investigated the decomposition of Ph_3Sb in oxygen by DSC method under the conditions identical to those employed in the degradation of PS. The DSC curve shows exotherm for oxidation process (Fig. 10). The temperature of the onset of thermo-oxidative degradation of Ph_3Sb is equal to 362.5°C.

Figures 1b and 3 show that the mixture of C_{60} with aromatic amine, phenyl-β-naphthylamine, has considerable synergistic effect in the thermo-oxidative degradation of PS. Further investigations are necessary for understanding the synergistic action of this mixture. It may be proposed that the components of the mixture react with each other with formation of more effective stabilizer.

4. CONCLUSION

In this study the effects of the double mixtures of fullerene C_{60} with well-known antioxidants (phenols, amines, S- and P-containing compounds and Ph_3Sb) on the temperature of the onset of the thermo-oxidative degradation of PS have been studied. We also investigated the influence of concentration of C_{60} on the value of T_0^{max} in the presence of various antioxidants.

It has been shown that the mixtures of C_{60} with Ph_3Sb and phenyl-β-naphthylamine have a synergistic effect upon T_0. Addition of C_{60} to these compounds leads to an increase in the values of T_0^{max} for Ph_3Sb and phenyl-β-naphthylamine.

The suggestion was made that in the case of mixtures of C_{60} with Ph_3Sb, the synergistic effect is associated with different mechanisms of stabilizing action of components on PS degradation, namely C_{60} reacts with alkyl and oxygen-containing radicals with the formation of more stable compounds, and Ph_3Sb decomposes polymeric and fullerene-containing peroxides and hydroperoxides.

It was concluded that further investigations are necessary for understanding the synergistic action of mixture of C_{60} with phenyl-β-naphthylamine in the thermo-oxidative degradation of PS.

Acknowledgements

The research described herein was conducted in the framework of the Russian Scientific and Technical Program "Fullerenes and Atomic Clusters" (project 3-8-98). The authors wish to thank Prof. A. V. Gutchin for supplying triphenylstibine and Ph.D. M. A. Lopatin for supplying fullerene.

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